# Fundamental treatment of molecular-dynamics ensembles

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In microcanonical molecular dynamics the conservation of total momentum implies that the trajectories generate an ensemble with constant total momentum. We present the exact statistical mechanics of this microcanonical molecular dynamics ensemble. Using the adiabatic invariant phase volume to define the entropy, exact formulas, containing thermodynamic response functions, are derived for the microcanonical molecular dynamics ensemble and a numerical comparison of these formulas is made with fluctuation formulas which are valid in the thermodynamic limit and often used in molecular dynamics. No significant difference is found between the results calculated using the different formulas for a system of 432 particles; however, for simulations with small numbers of particles or small-cluster studies, the differences could be important.

## I. INTRODUCTION

Molecular dynamics has become an important technique for studying the $N$-body problem in statistical mechanics. In the traditional form of molecular dynamics one has a fixed number $N$ of atoms occupying a fixed volume $V$ and interacting through a potential energy $U$. The system of atoms is described by the Hamiltonian $\mathcal{H}$,

$$\mathcal{H}=\sum_a \mathbf{p}_a^2/(2m)+U \ , \tag{1.1}$$

where $\mathbf{p}_a$ is the momentum of particle $a$. One solves for the motion of the atoms using Newton's laws, which are generated from this Hamiltonian. For many applications the potential depends only on the particle coordinates and possibly the system volume; the system energy $E=\mathcal{H}$ and total linear momentum $\mathbf{M}=\sum\mathbf{p}_a$ are four integrals of the motion.

The equilibrium statistical-mechanics ensemble describing the system with these four integrals of the motion is a special case of the microcanonical or $EVN$ ensemble; the $EVN$ microcanonical ensemble describes a system of $N$ particles in a volume $V$ with total energy $E$. For our system the additional constants of the motion represented by the total momentum $\mathbf{M}$ means that we are dealing with the $EVN\mathbf{M}$ ensemble. The fact that molecular dynamics generates an ensemble which is a special case of the microcanonical ensemble with constant total momentum was recognized in the paper by Lebowitz, Percus, and Verlet[1] and has been stressed by Wood[2] who named the ensemble the molecular-dynamics ensemble, a terminology which we shall employ in this paper. As will be discussed in detail later there are now several new forms of molecular dynamics which give rise to their respective molecular dynamics ensembles.[3]

Recent work on the molecular dynamics ensemble was initiated by Lado;[4] he showed, among other things, how to calculate exactly the density of states $\omega(E,V,N,\mathbf{M})$ for an ideal gas in the molecular-dynamics ensemble. In a later paper,[5] Wallace and Straub also discussed the molecular-dynamics ensemble.

The primary purpose of the present paper is to give the details of the exact statistical mechanics of the molecular dynamics, $EVN\mathbf{M}$, ensemble. In Sec. II we give a brief review of the statistical mechanics of the $EVN$ ensemble in order to establish our notation. Section III contains the definition and discussion of the $EVN\mathbf{M}$ ensemble. Included is the derivation of exact formulas used to determine thermodynamic response functions and a numerical comparison of results obtained with these formulas and the thermodynamic limit formulas widely used in molecular dynamics. Section IV contains a discussion of other microcanonical (constant total momentum) molecular-dynamics ensembles. Finally in Sec. V we present our conclusions. All of our discussions involve classical statistical mechanics, although many of the results have corresponding formulas in quantum statistical mechanics.

## II. SUMMARY OF THE EVN ENSEMBLE

For a system of $N$ particles occupying a volume $V$ and described by the Hamiltonian $\mathcal{H}(q,p)$ the phase-space volume is defined by

$$\Phi(E,V,N)=\int \Theta(E-\mathcal{H})d^{3N}q\, d^{3N}p/C_N \ , \tag{2.1}$$

where $E$ is the system energy, $\Theta$ is the step function defined so that the integral is only over the phase space inside the energy surface $\mathcal{H}=E$, and $C_N$ is a constant. The fundamental connection with statistical mechanics is given by relating the adiabatic invariant phase volume $\Phi$ to the thermodynamic entropy via the Boltzmann relation

$$S(E,V,N)=k_B\ln\Phi \ . \tag{2.2}$$

Expressions for various thermodynamic quantities follow by combining Eq. (2.2) and the differential thermodynamic relation

 

$$TdS = dE + PdV \ . \tag{2.3}$$

For example, the thermodynamic relations

$$T^{-1} = \left[\frac{\partial S}{\partial E}\right]_V \tag{2.4}$$

and

$$P/T = \left[\frac{\partial S}{\partial V}\right]_E \ , \tag{2.5}$$

can be used to calculate expressions for the temperature and pressure. Combining Eqs. (2.4) and (2.5) with Eq. (2.2) we obtain the statistical-mechanics relations

$$k_B T = \Phi/\omega \tag{2.6}$$

and

$$P = -\langle \partial \mathcal{H}/\partial V \rangle \ , \tag{2.7}$$

where the angular brackets indicate the microcanonical average value over the energy shell

$$\langle A(q,p) \rangle = \int A(q,p)\delta(E-\mathcal{H})d^{3N}q d^{3N}p/(\omega C_N) \tag{2.8}$$

for any phase-space function $A(q,p)$, and the density of states $\omega(E,V,N)$ is given by

$$\omega = \int \delta(E-\mathcal{H})dq^{3N}d^{3N}p/C_N \ , \tag{2.9}$$

$$\omega = \frac{\partial \Phi}{\partial E} \ . \tag{2.10}$$

If the potential energy $U$ depends on the spatial coordinates only then the momentum integrals in $\Phi$ and $\omega$ can be carried out by using the formulas for a sphere of radius $[2m(E-U)]^{1/2}$ of $3N$ dimensions as done by Münster[6] to yield

$$\Phi = \int (E-U)^{3N/2}\Theta(E-U)d^{3N}q/[C_0\Gamma(3N/2+1)] \ , \tag{2.11}$$

$$\omega = \int (E-U)^{3N/2-1}\Theta(E-U)d^{3N}q/[C_0\Gamma(3N/2)] \ , \tag{2.12}$$

where $C_0 = C_N/(2\pi m)^{3N/2}$ and $\Gamma$ is the gamma function. Similarly the ensemble average of any dynamical variable which depends only upon the spatial coordinates can be reduced from Eq. (2.8) to the form

$$\langle A \rangle = \int A(E-U)^{3N/2-1}\Theta(E-U)d^{3N}q/[\omega C_0\Gamma(3N/2)] \ . \tag{2.13}$$

As an example, if $A$ is the kinetic energy $K = E - U$ in Eq. (2.13), we obtain

$$\langle K \rangle = 3Nk_B T/2 \ , \tag{2.14}$$

where we have used Eq. (2.6). Using Eq. (2.5) along with Eq. (2.11) for $\Phi$ we obtain the equation of state

$$P = Nk_B T/V - \langle \partial U/\partial V \rangle \ . \tag{2.15}$$

As recently shown by Pearson, Halicioglu, and Tiller[7] various *exact* formulas, containing thermodynamic response functions, may be derived using thermodynamic relations and Eqs. (2.11) and (2.12). We shall illustrate the derivation of such formulas for the *EVN***M** ensemble later.

The definition of the entropy in terms of phase volume $\Phi$ [Eq. (2.2)] follows from the adiabatic invariance of the phase volume; this is presented in detail in Münster[6] and Becker.[8] After the entropy is introduced by Eq. (2.2), one shows that in the thermodynamic limit the entropy can also be calculated by using $k_B \ln\omega$ since[6]

$$\frac{\ln\Phi - \ln\omega}{N} \underset{N\to\infty}{\sim} O(N^{-1}\ln N) \ . \tag{2.16}$$

To compare the two different definitions of the entropy, we give the following examples corresponding to Eqs. (2.6), (2.14), and (2.15) obtained by using the expressions $S = k_B \ln\omega$ (Ref. 7):

$$\frac{1}{k_B T} = \frac{1}{\omega}\left[\frac{\partial \omega}{\partial E}\right]_V \ , \tag{2.6'}$$

$$\langle K^{-1} \rangle^{-1} = \left[\frac{3N}{2} - 1\right] k_B T \ , \tag{2.14'}$$

$$P = \frac{Nk_B T}{V} - \left\langle \left[\frac{\partial U}{\partial V}\right] K^{-1} \right\rangle \langle K^{-1} \rangle^{-1} \ . \tag{2.15'}$$

These equations lead to the customary *EVN* ensemble relations [Eqs. (2.6), (2.14), and (2.15)] in the thermodynamic limit. Note that the temperature $T$ in the canonical ensemble probability density, $e^{-\mathcal{H}/k_B T}$, is defined by Eq. (2.6'), where $\omega$ is associated with the thermal reservoir.[8] If $k_B \ln\omega$ were used for the entropy definition in this paper, then various formulas in Sec. III of this paper would be modified. We have chosen to use the phase volume $\Phi$ to define the entropy since $\Phi$ is an exact adiabatic invariant and its relationship to the entropy is, therefore, also exact. On the other hand, if $\omega$ is used to define the entropy then one is implicitly assuming the thermodynamic limit, Eq. (2.16).

## III. THE MOLECULAR DYNAMICS *EVN***M** ENSEMBLE

For the *EVN***M** ensemble one has the additional constraint of constant total momentum as discussed previously. In this case the phase volume is modified to the form

$$\Phi(E,V,N,\mathbf{M}) = \int \Theta(E-\mathcal{H})\delta\left[\mathbf{M}-\sum_a \mathbf{p}_a\right] d^{3N}q\, d^{3N}p\,/\bar{C}_N\ , \tag{3.1}$$

where $\bar{C}_N$ is a constant. The connection between the entropy and the phase volume is again given by Boltzmann's relation

$$S(E,V,N,\mathbf{M}) = k_B \ln\Phi\ . \tag{3.2}$$

Using the Laplace transform of the step function and the Fourier expansion of the $\delta$ function, the momentum integrals can be carried out in Eq. (3.1). After taking the inverse Laplace transform of the result, the following expression for $\Phi$ is obtained:

$$\Phi(E,V,N,\mathbf{M}) = \int \left[E-\frac{M^2}{2Nm}-U\right]^{3(N-1)/2} \times\Theta\left[E-\frac{M^2}{2Nm}-U\right] d^{3N}q \times\{\bar{C}_0\Gamma[3(N-1)/2+1]\}^{-1}\ , \tag{3.3}$$

where $\bar{C}_0=\bar{C}_N N^{3/2}/(2\pi m)^{3(N-1)/2}$. Then the phase space density $\omega=\partial\Phi/\partial E$ is

$$\omega(E,V,N,\mathbf{M}) = \int \left[E-\frac{M^2}{2Nm}-U\right]^{3(N-1)/2-1} \times\Theta\left[E-\frac{M^2}{2Nm}-U\right] d^{3N}q \times\{\bar{C}_0\Gamma[3(N-1)/2]\}^{-1}\ , \tag{3.4}$$

and the average of any dynamical variable $A(q)$ in the $EVN\mathbf{M}$ ensemble has the form

$$\langle A\rangle = \int A\left[E-\frac{M^2}{2Nm}-U\right]^{3(N-1)/2-1} \times\Theta\left[E-\frac{M^2}{2Nm}-U\right] d^{3N}q \times\{\omega\bar{C}_0\Gamma[3(N-1)/2]\}^{-1}\ . \tag{3.5}$$

Equations (3.3)–(3.5) should be compared with Eqs. (2.11)–(2.13) in Sec. II; one difference in these equations is that the dimension of the sphere is reduced by 3 in the $EVN\mathbf{M}$ ensemble phase volume and density-of-states formulas as compared to the $EVN$ formulas.

It is important to note that even in the limit when the total momentum is chosen to have the value zero, Eq. (3.1) does not reduce to the $EVN$ expression Eq. (2.1). Thus, the $EVN$ and $EVN\mathbf{M}$ ensembles produce different results in this limit.

The thermodynamic relation Eq. (2.4) leads to the same relation for the temperature as in the $EVN$ ensemble

$$k_B T=\Phi/\omega\ . \tag{3.6}$$

The average of the kinetic energy $K=E-U$ can be obtained from Eq. (3.5) and has the value

$$\langle K\rangle = 3(N-1)k_B T/2+M^2/(2Nm)\ . \tag{3.7}$$

Notice that for $\mathbf{M}=0$ the average kinetic energy in the $EVN\mathbf{M}$ ensemble differs from the $EVN$ result Eq. (2.14) by $N-1$ replacing $N$. Since molecular dynamics calculations are normally carried out with $\mathbf{M}=\mathbf{0}$ this means that one should use the relation

$$\langle K\rangle_{\mathbf{M}=0} = 3(N-1)k_B T/2 \tag{3.8}$$

to relate the temperature and kinetic energy. Thus, for a given kinetic energy the temperature is slightly higher than would be obtained using Eq. (2.14). Of course, this small difference is not of practical importance in most simulations.

The equation-of-state equation in the $EVN\mathbf{M}$ ensemble can be obtained from the thermodynamic equation (2.5) using the Boltzmann expression for the entropy and Eq. (3.3) for $\Phi$. In order to take the volume derivative of $\Phi$ it is convenient to scale the coordinates via $q'=q/V^{1/3}$ in Eq. (3.3) which puts $\Phi$ in the form

$$\Phi = V^N \int \left[E-\frac{M^2}{2Nm}-U\right]^{3(N-1)/2} \times\Theta\left[E-\frac{M^2}{2Nm}-U\right] d^{3N}q' \times\{\bar{C}_0\Gamma[3(N-1)/2+1]\}^{-1}\ . \tag{3.9}$$

Using Eq. (2.5) with this form for $\Phi$ leads to the equation of state

$$P = Nk_B T/V - \langle \partial U/\partial V\rangle\ . \tag{3.10}$$

Notice that this is the same as the $EVN$ result given by Eq. (2.15). Sometimes one sees Eq. (3.10) with $N$ replaced by $N-1$ in molecular dynamics papers; however, as we have shown here, the correct expression for the pressure in the $EVN\mathbf{M}$ ensemble is Eq. (3.10).

Using the methods developed in Ref. 7 we can derive exact formulas containing various thermodynamic response functions in the $EVN\mathbf{M}$ ensemble. These formulas may be used in molecular dynamics to calculate the relevant thermodynamic response functions. In the thermodynamic limit these exact formulas may be related to often used fluctuation formulas involving the same response functions. We shall present three such formulas: for the constant volume heat capacity $C_V$, the Grüneisen parameter $\gamma$, and the adiabatic bulk modulus $B_s$.

### A. Heat capacity

Using the thermodynamic relation

$$1/C_V = \left[\frac{\partial T}{\partial E}\right]_V\ , \tag{3.11}$$

along with Eqs. (2.6) and (3.3), for $\Phi$, we find the exact formula for the heat capacity in the $EVN\mathbf{M}$ ensemble

$$k_B/C_V = 1-[1-2/3(N-1)]\langle K\rangle\langle K^{-1}\rangle \ , \quad (3.12a)$$

where $\langle K^{-1}\rangle$ is the average of the inverse kinetic energy.

### B. Grüneisen parameter

Using the thermodynamic relation $\gamma = V(\partial P/\partial E)_V$ and our statistical-mechanics formulas we obtain the formula for the Grüneisen parameter

$$\gamma = [1-3(N-1)/2] \times V\left[\left\langle K^{-1}\frac{\partial U}{\partial V}\right\rangle - \langle K^{-1}\rangle\left\langle\frac{\partial U}{\partial V}\right\rangle\right] + \frac{Nk_B}{C_V} \ . \quad (3.12b)$$

### C. Bulk modulus

For the bulk modulus $B_s = -V(\partial P/\partial V)_s$ we obtain the formula

$$B_s = \frac{Nk_BT}{V}\left[1+2\gamma-\frac{Nk_B}{C_V}\right] + V\left\langle\frac{\partial^2 U}{\partial V^2}\right\rangle - (\tfrac{3}{2}(N-1)-1) \times V\left[\left\langle K^{-1}\left[\frac{\partial U}{\partial V}\right]^2\right\rangle - 2\left\langle K^{-1}\frac{\partial U}{\partial V}\right\rangle\left\langle\frac{\partial U}{\partial V}\right\rangle + \left\langle\frac{\partial U}{\partial V}\right\rangle^2\langle K^{-1}\rangle\right] . \quad (3.12c)$$

### D. General remarks and numerical calculations

If the factors of $N-1$ are replaced by $N$ in Eqs. 3.12(a)–3.12(c) these formulas are the same as the exact formulas obtained in Ref. 7 for the $EVN$ ensemble. In the thermodynamic limit, $N\to\infty$, Eqs. 3.12(a)–3.12(c) of the $EVN\mathbf{M}$ ensemble go over into the following fluctuation formulas[1,7,9] for the thermodynamic response functions:

$$Nk_B/C_V^{\infty} = \tfrac{2}{3} - N(\langle K^2\rangle - \langle K\rangle^2)/\langle K\rangle^2 \ , \quad (3.13a)$$

$$\gamma^{\infty} = \tfrac{3}{2}\frac{NV}{\langle K\rangle^2}\left[\left\langle K\frac{\partial U}{\partial V}\right\rangle - \langle K\rangle\left\langle\frac{\partial U}{\partial V}\right\rangle\right] + \frac{Nk_B}{C_V^{\infty}} \ , \quad (3.13b)$$

$$B_s^{\infty} = \frac{Nk_BT}{V}\left[1+2\gamma^{\infty}-\frac{Nk_B}{C_V^{\infty}}\right] + V\left\langle\frac{\partial^2 U}{\partial V^2}\right\rangle - \frac{V}{k_BT}\left[\left\langle\left[\frac{\partial U}{\partial V}\right]^2\right\rangle - \left[\left\langle\frac{\partial U}{\partial V}\right\rangle\right]^2\right] , \quad (3.13c)$$

where the $\infty$ superscript indicates the thermodynamic limit. The thermodynamic limit formulas [Eqs. 3.13(a)–3.13(c)] are the same in both the $EVN$ and $EVN\mathbf{M}$ ensembles.

In recent simulations of sodium enough data were saved on tape to give a detailed comparison of the results obtained with Eqs. 3.12(a)–3.12(c) and with Eqs. 3.13(a)–3.13(c) without doing any further molecular-dynamics calculations. The calculation used a system of 432 atoms arranged in a bcc lattice. The molecular-dynamics run was of duration 17.13 ps (25 000 iterations). The potential used to model the interaction between sodium atoms was a pseudopotential model constructed by Price, Singwi, and Tosi.[10] For these calculations we used $EVN\mathbf{M}$ molecular dynamics with $\mathbf{M}=0$. The comparison of results obtained using Eqs. (3.12) and (3.13) along with the experimental values[11–13] is shown in Table I. These results show, as we expected, that there is no practical difference between Eqs. (3.12) and (3.13) for this molecular-dynamics simulation.

## IV. OTHER MICROCANONICAL MOLECULAR-DYNAMICS ENSEMBLES

In the $EVN\mathbf{M}$ ensemble not only the volume but also the shape and size of the system are held rigid. If the system has the shape of parallelepiped spanned by the vectors **a**, **b**, and **c**, then we define a matrix $h$ by $h=(\mathbf{a},\mathbf{b},\mathbf{c})$. The microcanonical molecular-dynamics ensemble describing the system is the $Eh N\mathbf{M}$ ensemble. All the previous discussion relating to the $EVN\mathbf{M}$ ensemble is also valid for the $Eh N\mathbf{M}$ ensemble. Moreover, the $Eh N\mathbf{M}$ ensemble may be employed to discuss the statistical mechanics of anisotropic solids, e.g., the elas-

TABLE I. Comparison of the heat capacity, Grüneisen parameter, and bulk modulus calculated for sodium at 300 K using Eqs. (3.13) (exact) and Eqs. (3.12) (thermodynamic limit) along with the experimental values. The system consists of 432 atoms arranged in a bcc lattice interacting through a pseudopotential. The time over which these quantities were calculated was 17.13 ps and the system density was 0.97 g/cm$^3$. The experimental value of $C_V$ is obtained by using the $C_p$ value from Ref. 11 together with $B_T$ and $\gamma$ from Ref. 12.

| | $C_V$ (J/K mol) | $\gamma$ | $B_s$ (kbar) |
|---|---|---|---|
| Exact [Eqs. (3.13)] | 27.32±2.42 | 1.25±0.16 | 60.14±0.83 |
| Limit [Eqs. (3.12)] | 27.12±2.45 | 1.25±0.16 | 61.30±0.64 |
| Experimental | 25.99±0.12[a] | 1.27±0.04[b] | 67.7±0.6[b,c] |

[a]Reference 11.
[b]Reference 12.
[c]Reference 13.

tic properties of anisotropic solids. The *EhN* ensemble has been introduced in Ref. 3.

Over the past years molecular-dynamics methods have been developed to deal with constant pressure (Andersen[14]) and constant stress (Parrinello and Rahman[15]). These new ensembles are microcanonical ensembles with the enthalpy replacing the energy as the constant of the motion. Thus, we have Andersen's *HPN* ensemble and the *HtN* ensemble of Parrinello and Rahman; here $t$ is the thermodynamic tension tensor of the theory of finite elasticity.[3] When a microcanonical form of molecular dynamics is used the total momentum is held constant, usually having the value zero, and therefore one generates a microcanonical molecular-dynamics ensemble. The relevant statistical formulas for any of these new microcanonical ensembles can be developed along the same line as presented in Sec. III for the *EVN***M** ensemble. Thus, for example, we could work out the statistical mechanics of the *HPN***M** and *HtN***M** ensembles. The exact treatment of the *HPN* ensemble using the methods of Ref. 7 was presented by Ray and Graben.[16] We will leave the working out of the relevant statistical formulas for the *HPN***M** and *HtN***M** ensembles to the interested reader.

## V. CONCLUSIONS

In microcanonical molecular dynamics the conservation of the total momentum implies that the trajectories generate a molecular-dynamics ensemble with constant total momentum. We have developed the detailed statistical mechanics for the *EVN***M** ensemble and compared it with the usual *EVN* ensemble results. In this paper we have used the phase volume to define the entropy since this choice does not involve any discussion of the thermodynamic limit and allows one to derive exact expressions for thermodynamic response functions. As we have shown, factors of $N-1$ appear in various statistical formulas in the *EVN***M** ensemble. In the limit that the momentum is equal to zero the *EVN***M** ensemble does not reduce to the *EVN* ensemble. This means, for example, that the actual temperature in molecular-dynamics simulations, which are carried out with zero momentum, should be determined by Eq. (3.8) which gives a slightly higher temperature than the *EVN* result, Eq. (2.14). In actual simulations this difference would probably not be of much importance; however, one should be aware of the correct results and for simulations of small clusters the $N-1$ factors could be of importance.

We have also derived exact formulas for several thermodynamic response functions for the *EVN***M** ensemble and compared these to the exact *EVN* results and the the fluctuation formulas obtained in the thermodynamic limit. As Table I illustrates, the differences between the exact *EVN***M** formulas and the equations obtained in the thermodynamic limit are not of practical importance for the system investigated. However, again one should be aware of the correct expressions.

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